MICROCOPY RESOLUTION TEST CHART

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REPORT DOCUMENTATION PAGE		Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	

4. PERFORMING ORGANIZATION REPORT NUMBER(S) VSL-049/009-01	5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION Catholic Univ. of America	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code) Vitreous State Laboratory Washington, DC 20064	7b. ADDRESS (City, State, and ZIP Code) Physics Division--Code 1112 Arlington, VA 22217-5000

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-85-K-0500

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO. 61153N 11	PROJECT NO.	TASK NO. 4126939	WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)

A Molecular Dynamics Study of the Degradation of a Short Chain Polymer in a Dilute Solution Subjected to Severe Flow Conditions   (UNCLASSIFIED)

12. PERSONAL AUTHOR(S)

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13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 1 May 85 TO 30 Sep 86	14. DATE OF REPORT (Year, Month, Day) 1987 Feb 2	15. PAGE COUNT 36

16. SUPPLEMENTARY NOTATION

17.	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Drag Reduction, Polymer degradation, Molecular Dynamics, Strong flow

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

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(continued on reverse side)

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION
22a. NAME OF RESPONSIBLE INDIVIDUAL L. E. Hargrove	22b. TELEPHONE (Include Area Code) (202) 696-4221	22c. OFFICE SYMBOL ONR Code 1112

DD Form 1473, JUN 86   Previous editions are obsolete.   SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED

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OFFICE OF NAVAL RESEARCH

FINAL REPORT

for

1 May 1985 through 30 September 1986

for

Contract N00014-85-K-0500

R & T No. 4126939

A Molecular Dynamics Investigation of

the Mechanism of Turbulence Modification

by Polymer Additives and Noise Irradiation

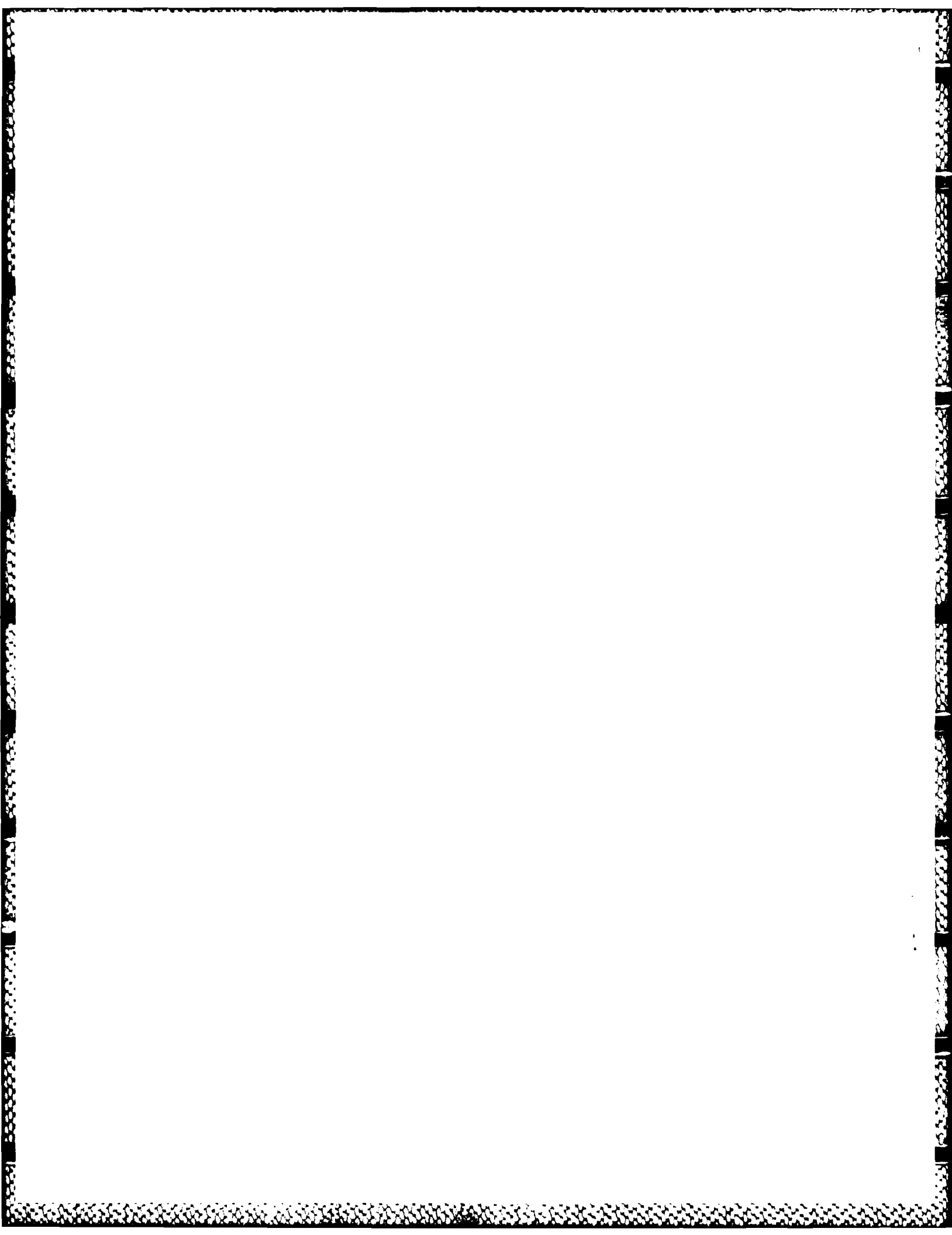Principal Investigators:

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A MOLECULAR DYNAMICS STUDY OF

THE DEGRADAT⁓ OF A SHORT CHAIN POLYMER

IN A DILUTE SOLUTION

SUBJECTED TO SEVERE FLOW CONDITIONS

by

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ABSTRACT

Molecular dynamics computer simulation "experiments" have been carried out to study the response of a dilute short-chain polymer solution subjected to severe flow conditions. Under high amplitude shear flows the polymer molecules were observed to reorient and reconfigure so as to be confined to a plane parallel to the flow direction. Once this situation is achieved, aperiodic cycling between coiled and elongated forms within the plane was observed. No significant enhancement of the intramolecular oscillations was seen, nor was there any flow-induced tension developed in the molecule. Conversely, in a configuration in which one end of the molecule was anchored and a uniform flow of solvent was maintained, scission of an intramolecular bond was found at high solvent flow velocities. The mechanism of bond rupture arose from the flow-driven excitation of intramolecular vibrational modes of motion of the molecule, the steady-state tension arising from viscous drag on the molecule being much smaller than that required for bond scission. Analysis of the flow-induced vibrations leads to the conclusion that bond breaking occurs only when there is substantial excitation of the low frequency acoustical modes of the molecule. This mechanism should also be operative in the degradation of very long-chain polymers in a flow field characterized by an extensional velocity gradient.

cause of the observed turbulent drag reduction by dilute concentrations of polymers.

Recent theories (Peterlin, 1970; Keller and Mackley, 1977; Hinch, 1977) suggest that extensional features of the turbulent flow and not the shear are the source of the reduced drag. These theories state that the phenomenon occurs because of interaction of polymer chains which are extended and aligned by the extensional components of the flow field. Indeed birefringence measurements (Pope and Keller, 1978; Crowley et al., 1976) have shown that extensional flows can extend and align randomly coiled polymers.

Unfortunately (for the practical application of this drag reduction effect) the extensional features of the flow also appear to be involved in the degradation of the polymers. For example, recent work (Odell et al., 1983; Merrill and Horn, 1984) has demonstrated near midpoint scission of polymer chains in a well characterized extensional flow. Near midpoint scission has been interpreted as implying that the molecule is nearly fully extended when it breaks; this conclusion is of course consistent with the birefringence data mentioned above.

The generally accepted model for this scission process visualizes a macromolecule as a string of beads aligned parallel to the flow field. Using Stokes law to calculate the drag on each monomer bead and a linear approximation of the acceleration at the point of maximum extensional strain rate, the maximum force on the central bead F_c can be calculated:

$$F_c = \frac{3}{4}\pi\eta R l \dot{\gamma}_e (M/M_0)^2, \tag{1}$$

MOLECULAR DYNAMICS

Molecular dynamics (MD) is a computer simulation technique in which one takes into account the many body nature of the microscopic dynamics by solving the classical equations of motion for the atoms of which a system is composed as a function of time (B. J. Alder and T. E. Wainwright, 1960; A. Rahman, 1964, 1966; L. Verlet 1967, 1968, 1970, 1973). One examines a system under certain given thermodynamic conditions (e.g., volume V, density N/V, total energy E), and assumes some model form(s) for the interactions (taken to be pairwise additive) among the atoms (whose masses are known) comprising the system. Using a finite difference stepwise procedure--in this work the Verlet algorithm was used--one then solves on a high speed computer for the positions and momenta of all the atoms in the system. From this record of the system's path through phase space one can obtain--measure--all the system properties that are amenable to study in conventional experiments as well as many that are not generally accessible.

In this work the system chosen for study consists of a monatomic liquid in which is dissolved a single linear "polymer" molecule. The solvent atoms interact via a Lennard-Jones (LJ) 6-12 potential function

$$\phi(r) = -4\epsilon \left[(\sigma/r)^6 - (\sigma/r)^{12} \right], \tag{2}$$

where r is the separation between the interacting atoms, and σ and ϵ are constant parameters, describing respectively, the molecular diameter of the interacting atoms and the depth of the attractive potential well. The atoms

contained in a cubical volume of edge length 10.5808 σ, giving a density (in reduced units) of $N\sigma^3/V = 0.8442$, the triple point density of a Lennard-Jones fluid. The reduced temperature (kT/ε, where k = Boltzmann's constant) was maintained at 0.722, the LJ fluid triple point temperature. This was achieved by scaling the random parts of the velocities of the N' solvent atoms at each time step such that a constant total kinetic energy

$$\frac{1}{2}N'mv^2 = \frac{3}{2}N'kT = \frac{3}{2}(992)(0.722) = 1074$$

is maintained for these atoms.

Periodic boundary conditions (or quasi-periodic boundary conditions in the cases when impressed flows are present) are employed to minimize the effects of the surface bounding the system. These are perhaps visualized most easily by considering the cubical region containing the system--the MD cell-- to be surrounded by replicas of itself. An atom that leaves the cell through any of its walls is replaced by its image that enters through the opposite wall.

The time step δt for the integration of the equations of motion was chosen as 1/512 of the basic LJ unit. This was chosen as it is more than an order of magnitude shorter than the smallest vibrational period of the polymer molecule or of any characteristic relaxation time of the solvent. Moreover in preliminary test runs in the absence of any impressed flow field and with the temperature control switched off, the constancy of the energy was maintained essentially the same as when a time step of 1/1024 the basic LJ unit was chosen.

scaling the solvent atom velocities) but no shear was impressed. At some instant of time, i.e., during one time step, the shear flow was established by adjusting the velocity of each solvent atom in the system and was then maintained constant for all subsequent times. The time evolution of such system properties as pressure, shear stress, and internal energy, among others was then determined. The behavior of the polymer molecule under these circumstances was also monitored as a function of time. This latter aspect was the focus of the work.

In rough outline the behavior is as follows. Prior to the imposition of the shear, the polymer exists in a highly "coiled" configuration. Following the switching on of the shear, the molecule initially straightens; this is shown in Figure 1 where the end-to-end distance is plotted as a function of time. As the molecule elongates it also aligns itself with the shear flow field. This is shown in Figure 2 where the projection of the end-to-end distance along the flow direction is shown. Once aligned with the flow direction, the driving force that produced the elongation disappears, and there is little tendency for the polymer to maintain this stretched-out configuration. Indeed, repetitive (if aperiodic) cycles of re-coiling, followed by subsequent elongation/alignment motions of the molecule are observed to occur. A time average of these configurations will show the polymer to have assumed a roughly ellipsoidal shape (the undisturbed configuration being essentially spherical) which will orient at a 45° angle relative to the flow (when the rotational part of the flow is taken into account) as sketched in Figure 3. This is consistent with the observations of flow-induced birefringence. There is little evidence of any enhancement of

energy in these internal modes waxes and wanes in time, fluctuating about some average value, characteristic of the particular flow rate. At the higher flow rates (solvent atom velocities $\geq$ 3.5) the molecule was observed to break at either the first or second bond. The mechanism that leads to this breaking will be discussed below.

The most obvious possibility is simply to assume that the mechanism of degradation is simply the growth of the static tension across the molecule to the point where the extensional force in bond number 1 exceeds the breaking strength of 1000. Assuming that the polymer is completely elongated and exactly aligned with the flow, one expects the viscous drag of the fluid on each of the atoms (denote this force by F_v) to be the same, and consequently the total force extending bond one should be approximately

$$F_{1T} = (N'' - 1) F_v = (N'' - 1) \zeta v_f \qquad (4)$$

Direct computations of F_T indicate that even at the highest flow rates examined, these static extensional forces are much less than the breaking force, and thus some alternative mechanism for the scission must be sought. Of course it is clear that for longer polymers the static extensional force will increase since F_{1T} is approximately proportional to N''. As a test of this idea a run with a larger system employing an extended 16-atom polymer was carried out with a solvent flow velocity of 3.5. Comparing this with runs under the same conditions for an eight-atom polymer gave values of F_{1T} (averaged over the duration of the runs) that were roughly twice as large for the 16-atom polymer system--$F_{1T}(16) \approx 160$ vs. $F_{1T}(8) \approx 75$. However, it is also clear that very long molecules will not adopt a fully extended configuration, but rather will assume a shape resembling the ellipsoidal form

degradation was observed for the short-chain (eight-atom) polymer system for flow velocities less than 3.5. For flow velocities $\geq$ 3.5, molecular bonds are ruptured even though (as was mentioned above) the viscous extensional forces are less than the bond strengths. To explain these results we adopt the following working hypothesis:

> Because the specific interatomic forces through which the polymer molecule interacts with the solvent atoms are not constant in time, but rather include a substantial random fluctuating component, the internal acoustical vibrational modes of motion of the molecule can be coupled to the flow energy. As energy is transferred into these internal degrees of freedom, there will occur situations in which the mode amplitudes are sufficiently large and the dynamical vibrations are appropriately phased to produce a stretching of a given bond that exceeds its maximum allowable extension (0.02). In such circumstances the bond breaks.

Characteristic data for the flow-velocity=3.0 run and the longer of the flow-velocity=3.5 runs are presented below. These runs (labeled A and B respectively) are chosen for analysis as they are reasonably typical of the cases where the polymer remains intact (Run A), and where there is polymer degradation (Run B). The initial states for these runs were quite different. In Run A the configuration was one in which the initial vibrational energy of the polymer molecule was somewhat higher than its equilibrium value, while in Run B, this energy was unusually low. Figures 4 and 5 respectively give the results for the elastic forces $F_1(t)$ in bond number one (the bond that broke in Run B) for these two cases.

$$\tilde{F}_n(\nu,\tau) = |\int_{\tau-1}^{\tau+1} dt\ e^{-2\pi i\nu t}\ F_n(t)\ | \qquad (5)$$

gives the dynamical response of each bond as a function of frequency, allowing

one to do an analysis of how the excitation of each normal mode of motion of

the polymer varies in time. Consider for example the results presented in

Figures 6 through 9. In these are shown the Fourier transforms for each bond

at two different time intervals; Figures 6 and 7 give results for Run A.

Figures 8 and 9 for Run B (a complete set of graphs showing these data at

additional time intervals can be obtained by writing directly to the authors

of this report). Taken as a group these graphs indicate that excitation is

confined principally to seven main frequency bands. These are listed below in

Table 2 along with the calculated longitudinal normal mode frequencies for a

linear chain of seven equal masses ($m = 1$) connected to one another and to a

rigid wall by identical springs ($K = 60,000$). As is evident, except for the

lowest frequency mode, there is rather reasonable agreement between the

calculated eigenfrequencies and the locations of the excitation bands. That

the bands are split into several components most likely results from the

polymer not being a simple one-dimensional system, and thus other degrees of

freedom contribute to the motion. The interaction of these with the

vibrational modes produces the complicated structure (splittings, line

broadening, ...) of the bands. The not inconsiderable amount of low frequency

and interband activity that is apparent in Figures 6 through 9 represents non-

resonant driving of the molecular system by the flowing liquid. If the

solvent-polymer interactions are viewed as arising from impulsive collisional

forces (the significant Fourier components in these interactions lie in the

$$\nu = \frac{1}{2\pi}\sqrt{K/m} = \frac{1}{2\pi}\sqrt{50000/7} \approx 13.5$$

which is certainly in the direction and of the proper order of magnitude of the observed frequency shift.

The total extent of the excitation in each mode for the various time intervals over which Fourier analyses were carried out was measured by integrating over each band. We define the excitation amplitude for the nth band as

$$A_n(\tau) = \int_{\nu_{n,min}}^{\nu_{n,max}} d\nu \, \widetilde{F}_n(\nu,\tau) \tag{6}$$

where $\nu_{n,min}$ and $\nu_{n,max}$ are respectively the minimum and maximum frequencies for the nth band as listed in Table 2. Plots of the excitation amplitudes for all the bands as functions of time for runs A and B are shown in Figures 10 and 11.

It is clear from the Run B data that scission occurs, i.e. that the bond is extended by 0.02, or equivalently that an extensional force $\geq$ 1000 develops in the bond, only after there is a rather sizeable buildup in the energy in the low frequency modes. For the particular run shown there is also growth of the energy in the other modes, and, insofar as each of these contributes not unimportantly to the force that stretches bond one, their contributions cannot be ignored. In other cases where a bond other than the first ruptured, the role of the higher frequency modes seemed to be less crucial. For instance, in the flow-velocity = 4.0 run, where scission occurred at the third bond, there was relatively little energy in the second and fifth excitation bands. Since the modes corresponding to these bands are characterized by rather small

SUMMARY

The principal result of this research effort is the finding that when neighboring elements of a flexible molecule are subjected to different solvent flow velocities, bond rupture can occur even though the steady-state tension in the bond is substantially less than the force required to break it.

In the model system considered in this work, bond scission results from excitation of acoustical or longitudinal vibrational modes of the molecule by the flowing solvent (after it has been extended by the flow field). In sufficiently strong flows, the amplitudes of the excited modes transiently superimpose at a particular bond, causing the instantaneous force of elongation in that bond to exceed its strength. In all the situations studied, a rather large degree of excitation of the lowest frequency mode was a necessary condition for the rupture of the bond. This is reasonable when it is recognized that the critical requirement is the driving of those modes which contribute importantly to the tension in a particular bond. For the specific configuration of a linear chain molecule anchored at one end and subjected to a uniformly flowing solvent, the lowest frequency mode is characterized by relatively large extensions of the bonds near the pinned end of the molecule; these were the locations of the scissions in the experiments reported here.

In experiments in which very long polymers (composed of hundreds or thousands of monomeric units) in an extensional flow field have been observed to degrade, a similar mechanism should also be operative. If the extensional flow is described by a constant velocity gradient, then the lowest frequency acoustical mode will correspond to a situation in which there is maximum

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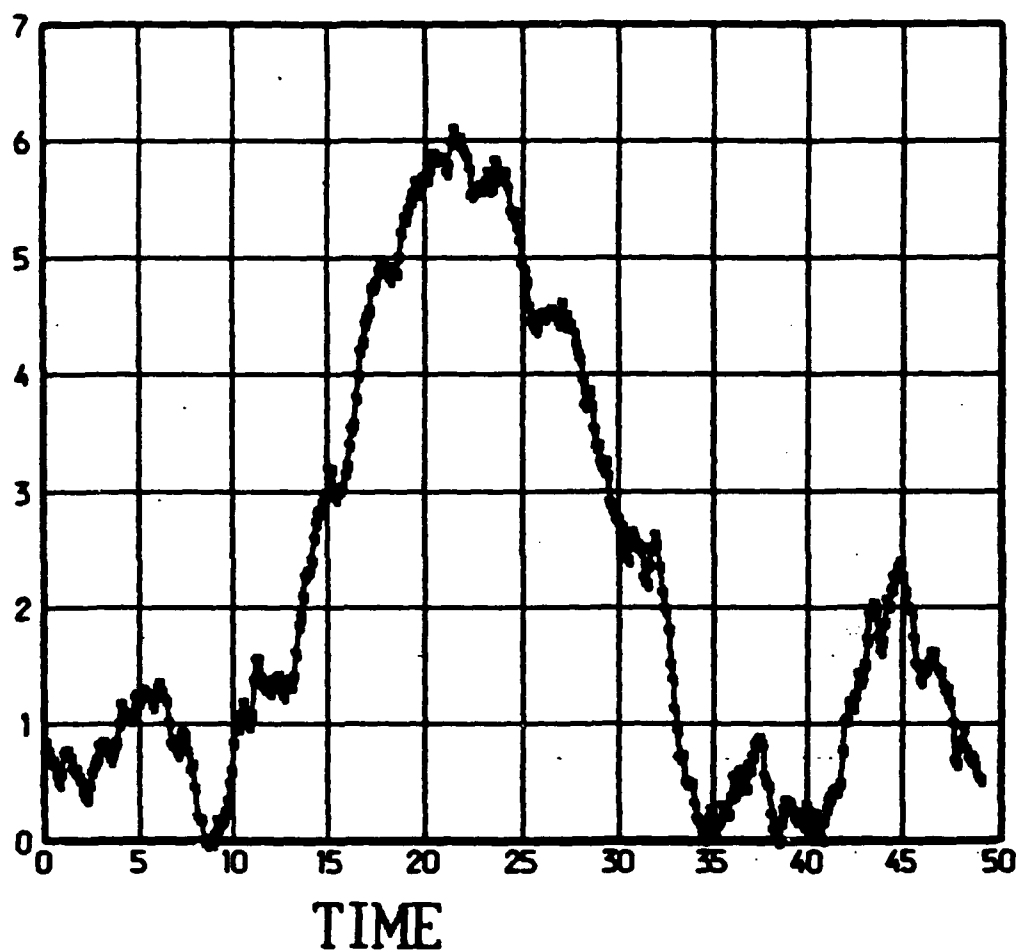LIST OF FIGURES (CONTINUED)

Figure 2. The behavior of the polymer end-to-end distance (absolute value) projected along the flow direction as a function of time. The conditions are the same as in Figure 1, i.e., a shear rate of 0.5 switched on at the time instant t = 3.75.
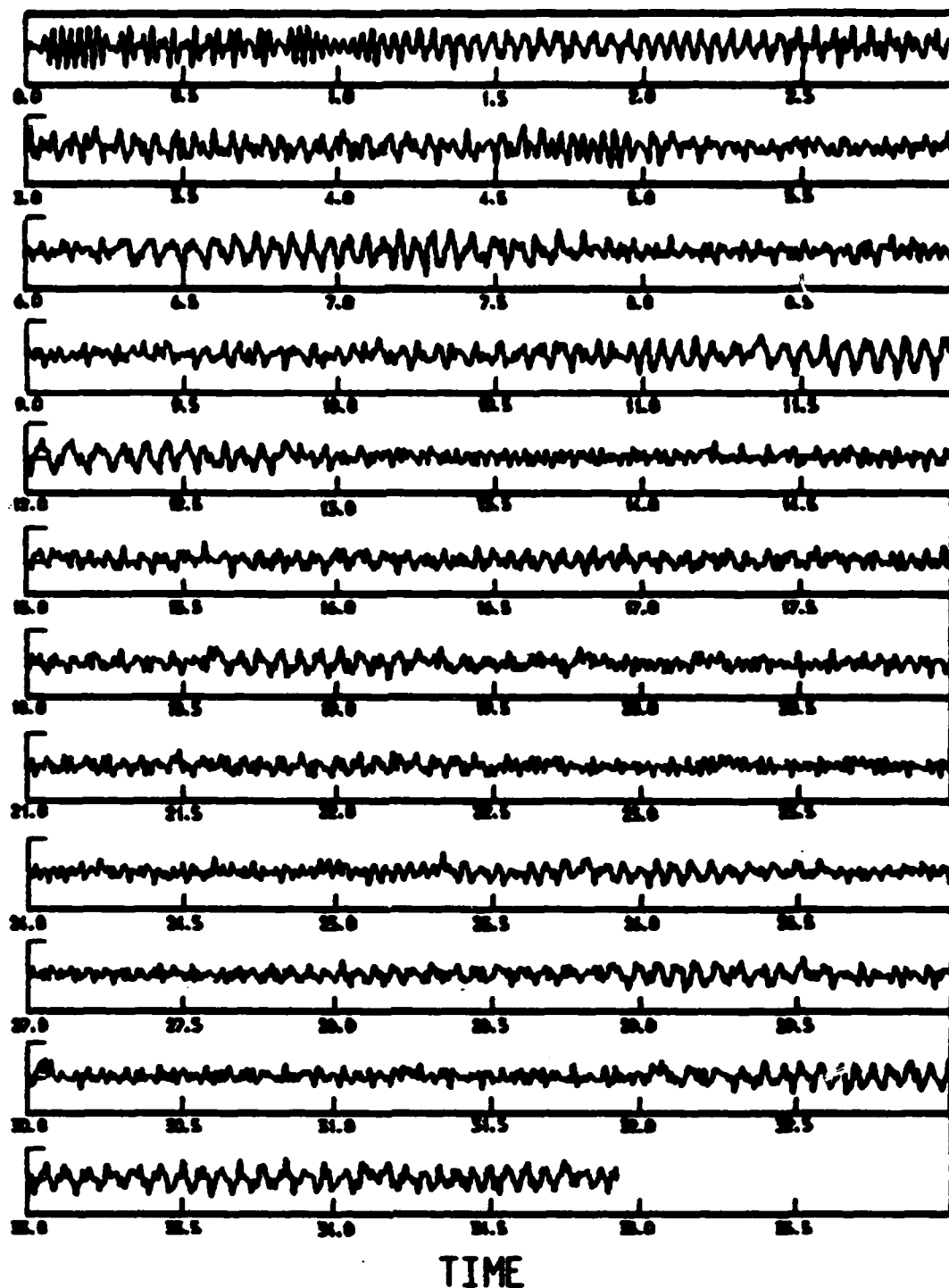
Figure 4. The restoring force (bond elongation times K) for bond number one as a function of time following the switching on of a solvent flow velocity of 3.0 (Run A). Beginning at the top, the horizontal tracings represent consecutive time intervals, each of 3 units, extending for a total duration of 35 units. The tick marks on the vertical axis correspond to a restoring force of 1000, the value at which the bond would break.
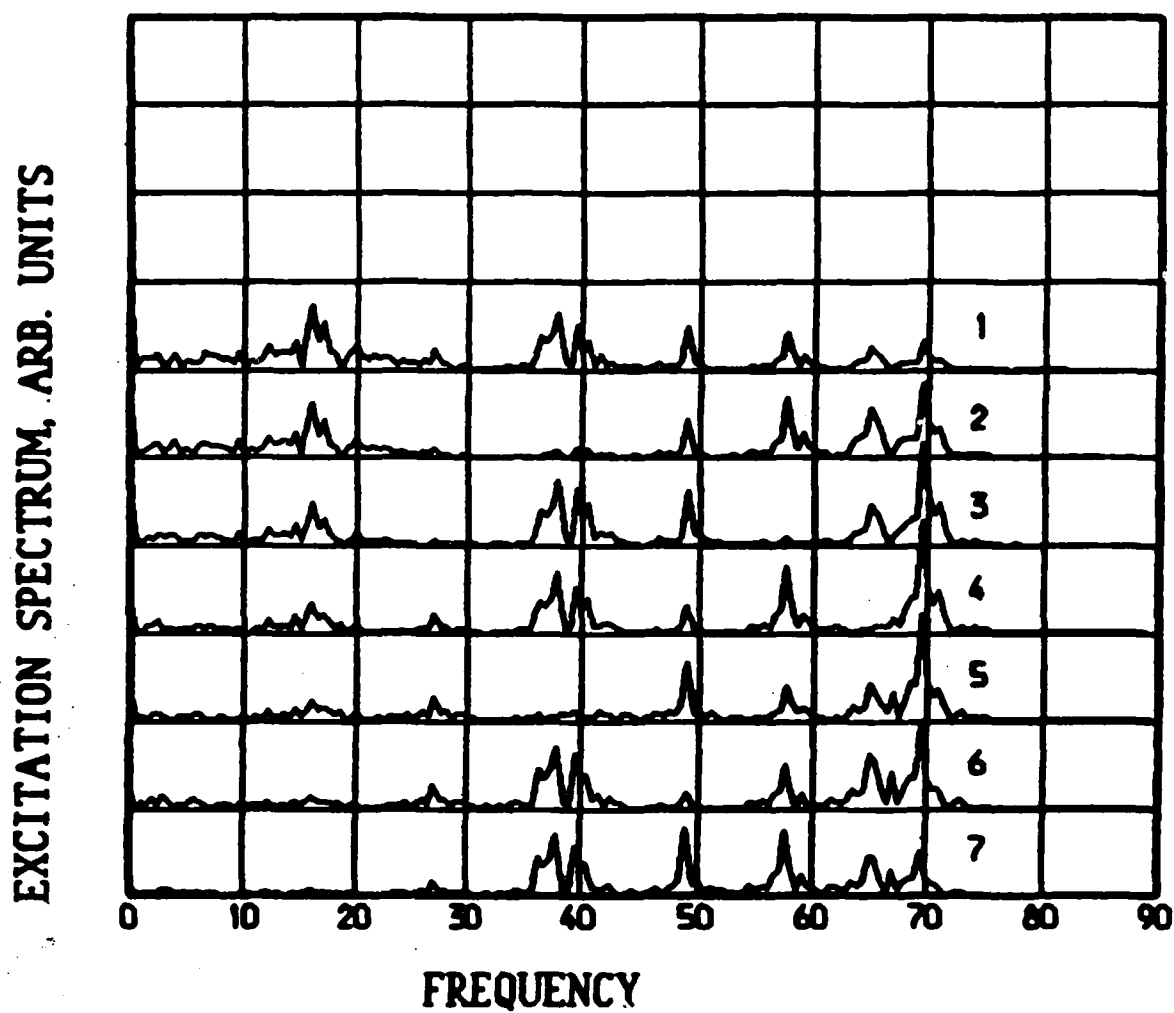
Figure 6. The Fourier transforms $\bar{F}_n$ defined in Eq. (5) for n = 1 to 7 computed at time $\tau = 21.81$ following the switching on of a flow velocity of 3.0 (Run A).
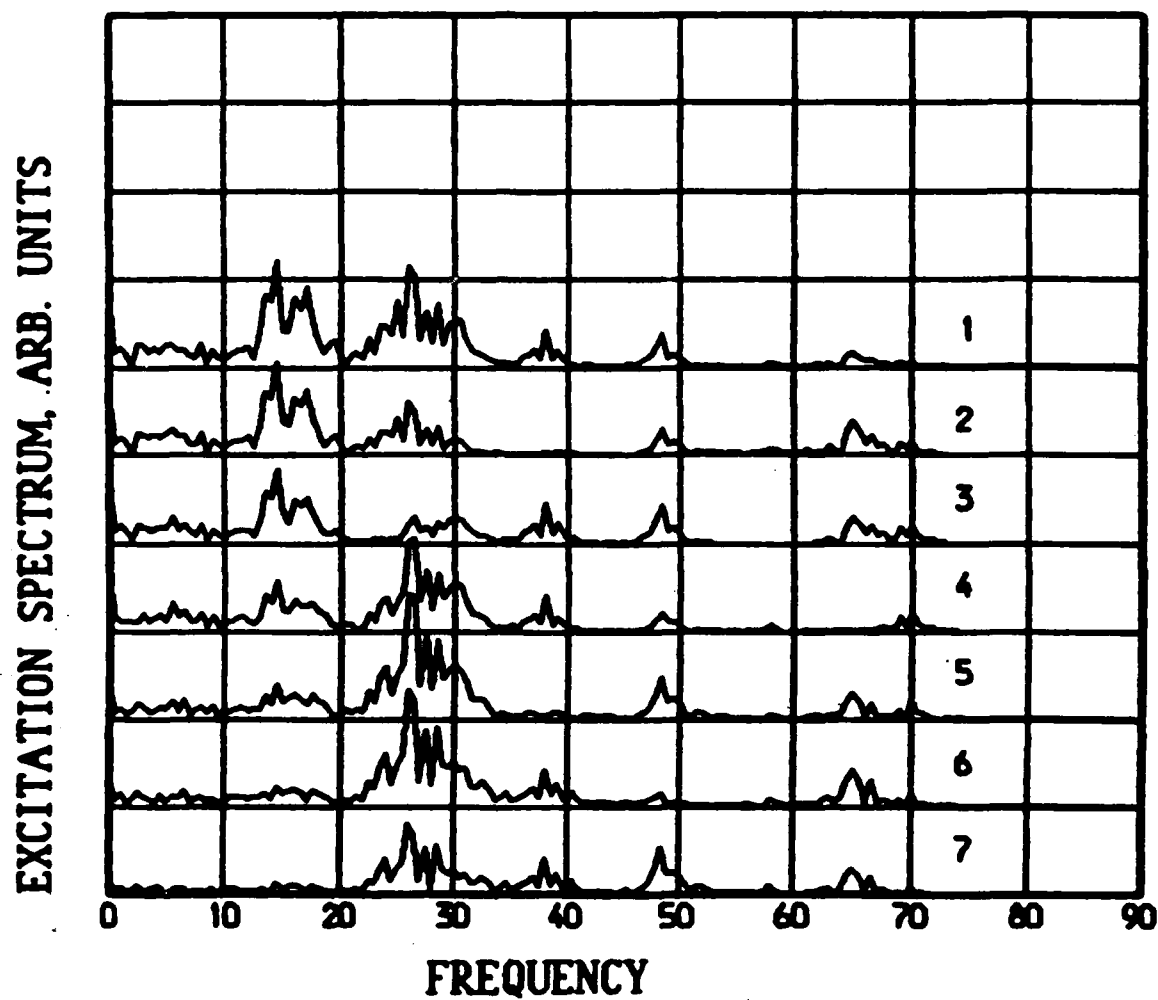
Figure 8.   The Fourier transforms $\bar{P}_n$ defined in Eq. (5) for n = 1 to 7 computed at time τ = 21.81 following the switching on of a flow velocity of 3.5 (Run B).
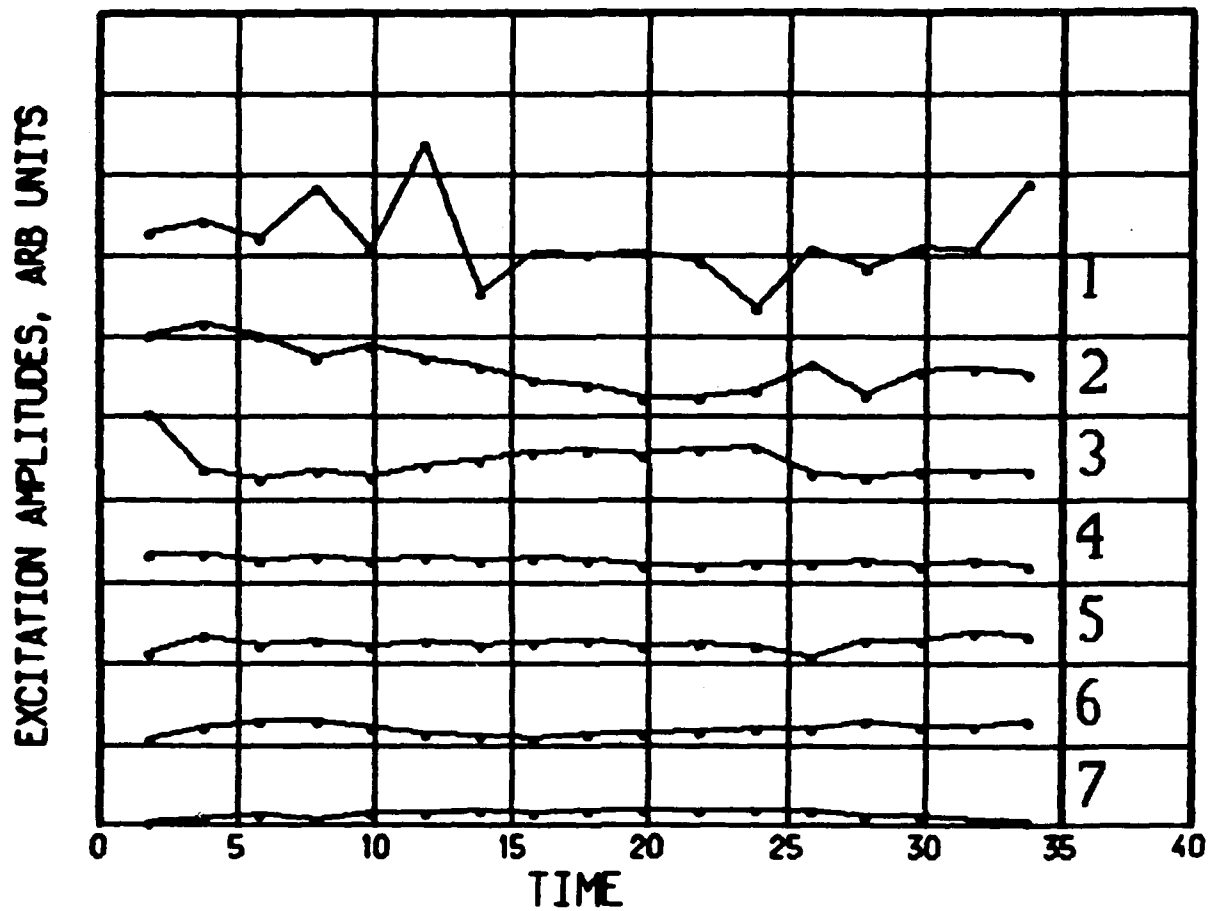
BOND NUMBER 1

Figure 10.   The time evolution of the excitation amplitudes defined in
            Equation (6) for the seven excitation bands following the switching
            on of a flow velocity of 3.0 (Run A).

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